

Application No. 09/549,918
Reply to Office Action of May 29, 2003

REMARKS

Claims 1-2 and 4-15 are currently pending in the application.

At the outset, it is noted that, upon reconsideration, the Examiner has withdrawn the restriction requirement thereby reinstating claims 7-9. However, since withdrawn claim 15 directly depends from claim 7, Applicants understand claim 15 to also be reinstated. Thus, the Examiner has incorrectly indicated in the Office Action (Paper No. 17) that claims 1-2 and 4-14, and not claims 1-2 and 4-15, are pending in the application. Applicants respectfully request the proper disposition of the claims be reflected in the next written Office Action.

It is also noted that contemporaneous with the filing of this Amendment, Applicants have filed a Supplemental Information Disclosure Statement. It is respectfully requested that the Examiner initial and return to the undersigned the PTO/SB/08A Form, indicating that the references cited therein have been considered.

In Paper No. 17, the Examiner has rejected claims 1-2 and 6-14 under 35 U.S.C. §102(e) as anticipated by or, in the alternative, under 35 U.S.C. §103(a) as obvious over U.S. Patent No. 6,524,550 B1 of Chintawar, et al. ("Chintawar"). The Examiner asserts that Chintawar discloses the invention substantially as claimed. The Examiner adds that Chintawar discloses zirconium oxide having a surface area of about 50 m²/g.

Importantly, the Examiner points out that Chintawar has an effective filing date of May 3, 1999, which is after Applicants' priority filing date of April 22, 1999. However, the Examiner notes that there is not a certified English translation of Applicants' priority document (Japanese Application No. Hei 11-115101) of record and, therefore, Chintawar is properly available as a prior art reference since its effective filing date is before the actual filing date of this application (April 14, 2000).

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In response, Applicants direct the Examiner's attention to the verified English translation of Japanese Application No. Hei 11-115101, attached hereto as Exhibit A, and respectfully request that it be made of record in this application. In consideration thereof, Applicants assert that, since claims 1-2 and 6-14 are supported by this priority document, the present application is entitled to a priority date of April 22, 1999. Thus, Chintawar is no longer properly available as a prior art reference since its effective filing date of May 3, 1999 is after Applicants' priority date of April 22, 1999. Accordingly, reconsideration and withdrawal of the Examiner's rejection of claims 1-2 and 6-14 are respectfully requested. Since claims 4-5 depend from claim 1, either directly or indirectly, reconsideration and withdrawal of the Examiner's objection of claims 4-5 as being based on a rejected parent claim are also respectfully requested.

The Examiner has rejected claims 7-9 under §103(a) as being obvious over U.S. Patent No. 5,030,440 of Lywood, et al. ("Lywood") in view of either U.S. Patent 6,110,862 of Chen, et al. ("Chen") or U.S. Patent No. 6,103,660 of Yperene, et al. ("Yperene") for the reasons given in the Office Action dated January 15, 2003 (Paper No. 14). Similarly, the Examiner has rejected claims 7-9 as being obvious over U.S. Patent No. 3,872,025 of Singleton in view of either Chen or Yperene for the reasons given in Paper No. 14. In support of these rejections, the Examiner paraphrases Applicants' argument in support of claim 1, in the Amendment filed April 15, 2003, that none of the cited prior art references teaches or suggests a shifting catalyst body comprising a carrier composed of titanium oxide and platinum supported thereon, or a catalyst body that comprises cerium oxide or zirconium oxide, and asserts that claims 7-9 do not require such a catalyst body.

Applicants have amended claim 7 such that claim 7 now recites, in part, that the shifting catalyst body comprises a carrier composed of at least one metal oxide selected from the group consisting of Ce, Zr and Ti, having a BET specific surface area of at least 10 m²/g and Pt

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supported thereon. Support for this amendment is found in original claims 3 and 4 and in the specification at, for example, page 5, lines 12-15. Therefore, no new matter has been added, and entry of the amendment is respectfully requested.

As stated in the April 15, 2003 Amendment, the cited prior art references do not teach, suggest, provide a motivation for, or a reasonable expectation of success from such a catalyst body. Thus, in consideration of the amendment to claim 7 and Applicants' earlier arguments in support of claim 7, the method of the invention, as now recited in claim 7, is not obvious in view of the cited prior art references. It follows that, since claims 8-9 and 15 all depend directly from claim 7, claims 8-9 and 15 are also not obvious in view of the cited prior art references. Accordingly, reconsideration and withdrawal of the Examiner's rejection of claims 7-9 are respectfully requested.

In view of the foregoing amendment and remarks, Applicants submit that pending claims 1-2 and 4-15 are patentably distinct from the prior art. Accordingly, reconsideration and withdrawal of the rejections and an early Notice of Allowance are respectfully requested.

Respectfully submitted,

KIYOSHI TAGUCHI *ET AL.*

(Date) 8/13/03 By: *William C. Youngblood*
WILLIAM C. YOUNGBLOOD
Registration No. 50,524
AKIN GUMP STRAUSS HAUER & FELD LLP
One Commerce Square
2005 Market Street, Suite 2200
Philadelphia, PA 19103-7013
Telephone: 215-965-1200
Direct Dial: 215-965-1246
Facsimile: 215-965-1210
E-Mail: wyoungblood@akingump.com

WWS:WCY:cas

Enclosure (Exhibit A- Verified English Translation of Japanese App. No. Hei 11-115101)

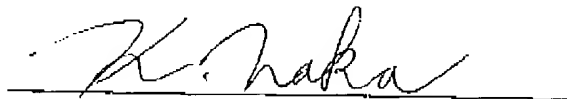
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Exhibit A

D E C L A R A T I O N

I, Koichi NAKA of 19-16, Daiwanishi 2-Chome,
Kawanishi-shi, Hyogo 666-0112 Japan hereby declare that I
am conversant with the Japanese language and that I am the
translator of the document attached and certify that to the
best of my knowledge and belief the following is a true and
correct English translation of the specification contained
in the Priority Document No. 11-115101.

This 14th day of July 2003



Koichi NAKA

Hei 11-115101
(Translation)

[DOCUMENT NAME] Patent Application
[REFERENCE NUMBER] 2033710031
[ADDRESSEE] To: The Commissioner of the Patent Office
[INTERNATIONAL PATENT CLASSIFICATION] C01B 3/58
[TITLE OF THE INVENTION] Hydrogen Refinement Apparatus
[INVENTOR]
 [DOMICILE OR RESIDENCE] c/o Matsushita Electric Industrial Co., Ltd.
 1006, Oaza-Kadoma, Kadoma-shi, Osaka-fu
 [NAME] Kiyoshi TAGUCHI
[INVENTOR]
 [DOMICILE OR RESIDENCE] c/o Matsushita Electric Industrial Co., Ltd.
 1006, Oaza-Kadoma, Kadoma-shi, Osaka-fu
 [NAME] Takeshi TOMIZAWA
[INVENTOR]
 [DOMICILE OR RESIDENCE] c/o Matsushita Electric Industrial Co., Ltd.
 1006, Oaza-Kadoma, Kadoma-shi, Osaka-fu
 [NAME] Kunihiro UKAI
[INVENTOR]
 [DOMICILE OR RESIDENCE] c/o Matsushita Electric Industrial Co., Ltd.
 1006, Oaza-Kadoma, Kadoma-shi, Osaka-fu
 [NAME] Toshiyuki SHONO
[INVENTOR]
 [DOMICILE OR RESIDENCE] c/o Matsushita Seiko Co., Ltd.
 6-2-61, imafukunishi, Joto-ku,
 Osaka-shi, Osaka-fu
 [NAME] Kouichiro KITAGAWA
[PATENT APPLICANT]
 [ID NUMBER] 000005821
 [DOMICILE OR RESIDENCE] 1006, Oaza-Kadoma, Kadoma-shi, Osaka-fu
 [NAME OR CORPORATE NAME] Matsushita Electric Industrial Co., Ltd.

[ATTORNEY]

[ID NUMBER] 100072431

[PATENT ATTORNEY]

[NAME OR Kazuo ISHII

CORPORATE NAME]

[INDICATION OF OFFICIAL CHARGE]

[NUMBER IN PRE-PAYMENT REGISTER] 066936

[AMOUNT PAID] ¥21,000

[LIST OF DOCUMENTS SUBMITTED]

[TITLE OF DOCUMENT] Specification 1

[TITLE OF DOCUMENT] Drawing 1

[TITLE OF DOCUMENT] Abstract 1

[NUMBER OF GENERAL POWER OF ATTORNEY] 9301762

[NECESSARY OR NOT OF PROOF] Necessary

Hei 11-115101

(Translation)

[DOCUMENT NAME] Specification

[TITLE OF THE INVENTION] Hydrogen Refinement Apparatus

[CLAIMS]

[Claim 1] A hydrogen refinement apparatus comprising a feeding part for a reformed gas containing at least a hydrogen gas, a carbon monoxide and steam, and a reaction chamber equipped with a carbon monoxide shifting catalyst body positioned downstream from said reformed gas feeding part, characterized in that said carbon monoxide shifting catalyst body comprises a carrier composed of at least one metal oxide and/or composite metal oxide having a BET specific surface area of $10 \text{ m}^2/\text{g}$ or more and Pt supported thereon.

[Claim 2] The hydrogen refinement apparatus in accordance with claim 1, characterized in that said metal oxide and/or composite metal oxide is an oxide of at least one selected from the group consisting of Mg, Al, Si, Ca, Ti, Cr, Fe, Zn, Y, Zr, Nb, Mo, Sn, Ba and lanthanoid.

[Claim 3] The hydrogen refinement apparatus in accordance with claim 2, characterized in that said metal oxide and/or composite metal oxide is at least one selected from the group consisting of alumina, silica, silica alumina, zirconia, titania and zeolite.

[Claim 4] The hydrogen refinement apparatus in accordance with claim 1 or 2, characterized in that said

composite metal oxide contains Ce.

[Claim 5] The hydrogen refinement apparatus in accordance with claim 1 or 2, characterized in that said metal oxide is cerium oxide.

[Claim 6] The hydrogen refinement apparatus in accordance with one of the claims 1 to 3, characterized in that said composite metal oxide contains Zr.

[Claim 7] The hydrogen refinement apparatus in accordance with one of the claims 1 to 6, characterized in that said carbon monoxide shifting catalyst body supports Pd, Rh or Ru in an amount of 0.1 to 0.5% by weight based on Pt, in addition to Pt.

[Claim 8] The hydrogen refinement apparatus in accordance with one of the claims 1 to 7, characterized in that said carrier is constituted of a heat-resistant inorganic metal material.

[Claim 9] The hydrogen refinement apparatus in accordance with one of the claims 1 to 8, characterized in that the temperature of said carbon monoxide shifting catalyst body carrier is controlled from 150 to 450°C.

[Claim 10] The hydrogen refinement apparatus in accordance with one of the claims 1 to 9, characterized in that the temperature of the upstream side part is controlled to be higher than the temperature of the downstream side part in said carbon monoxide shifting catalyst body.

[Claim 11] The hydrogen refinement apparatus in

accordance with one of the claims 1 to 10, characterized in that said reformed gas to be fed contains steam in an amount of 24 to 50% by volume.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Technical Field to Which the Invention Belongs]

The present invention relates to a hydrogen refinement apparatus, which refines a reformed gas containing hydrogen as the main component and, in addition, CO and provides a hydrogen gas of high purity.

[0002]

[Prior Art]

As the hydrogen source for a fuel cell, a reformed gas obtained by reforming a hydrocarbon, an alcohol, an ether or the like is used. In the case of a solid polymer fuel cell operating at a lower temperature of 100°C or less, there is a fear that a PT catalyst used in an electrode is poisoned by CO contained in the reformed gas. When a PT catalyst is poisoned, the reaction of hydrogen is disturbed and the power generation efficiency of the fuel cell decreases remarkably, therefore, it is necessary to remove CO to the CO concentration of 100 ppm or less, preferably 10 ppm or less.

Usually, for removal of CO, CO and steam are shift reacted for conversion into carbon dioxide and hydrogen to reduce the CO concentration to about several thousands ppm to about 1% in a CO shifting part equipped with a CO shifting

catalyst body. After that, a slight amount of air is added to remove CO to about several ppm level causing no bad influence on the fuel cell by a CO selective oxidation catalyst body.

Herein, for sufficient removal of CO, it is necessary to charge oxygen in an amount of 1 to 3-fold of the CO concentration, but hydrogen is also consumed in an amount corresponding to the amount of oxygen. That is, when the CO concentration is high, the amount of oxygen to be added increases and hydrogen to be consumed also increases, thus the efficiency of the whole apparatus reduces significantly. Therefore, it is necessary to decrease CO sufficiently in the CO shifting part.

[0003]

Conventionally, there have been used, as the CO shifting catalyst, copper-zinc-based catalysts, copper-chromium-based catalysts and the like for lower temperatures, which can be used at 150 to 300°C and iron-chromium-based catalysts and the like for higher temperatures, which can function at 300°C or more. These CO shifting catalysts have been used singly, or combinations of CO shifting catalysts for higher temperatures and for lower temperatures, depending on the use for chemical plants, hydrogen generating apparatuses for fuel cell and the like.

When above-mentioned copper-based CO shifting catalysts for lower temperatures are used as the main catalyst, extremely high catalytic activity is obtained, however, there

is a need to perform reduction treatment before use to give activation. Furthermore, due to heat generation during the activation treatment, it has to be treated over a long period of time while controlling the feeding amount of a reduction gas, for example, so that the temperature of the catalyst does not exceed the heat-resistant temperature.

[0004]

Also, since there is a possibility that a CO shifting catalyst once activated is re-oxidized and deteriorated in the case oxygen is introduced when stopping the apparatus and the like, measures are required such as prevention of oxidation.

Moreover, since the CO shifting catalyst for lower temperatures has low heat resistance and the catalyst cannot be heated acutely in starting the apparatus, a measure is needed to increase the temperature gradually.

On the other hand, when only the CO shifting catalyst for higher temperatures is used, there is no problem when the temperature increases somewhat excessively due to high heat-resistance thereof, thus it is easy to be heated in starting.

However, since the CO shifting reaction is an equilibrium reaction depending on temperature, when a CO shifting catalyst functioning only at higher temperatures is used, it is difficult to control the CO concentration to 1% or less. Therefore, there is a problem that purification efficiency lowers in a CO purification part that later connects.

[0005]

[Problem That the Invention Is to Solve]

As described above, in the prior art, a longer time is necessary for activation of a shifting part in a hydrogen generating apparatus and handling is complicated, therefore, there is a problem that it cannot be applied sufficiently for frequent repetition of starting-up and stopping.

Accordingly, in order to solve above-mentioned problems, an object of the present invention is to provide a hydrogen refinement apparatus (which is corresponded to a so-called shifting part), in which activation treatment of a CO shifting catalyst is easy and influences by oxygen introduction during the repetition of starting-up and stopping of operation are decreased to operate stably for a longer period of time.

[0006]

[Means for Solving the Problem]

In order to solve above-mentioned problems, the present invention relates to a hydrogen refinement apparatus comprising a reformed gas feeding part containing at least a hydrogen gas, carbon monoxide and steam, and a reaction chamber equipped with a carbon monoxide shifting catalyst body positioned downstream from said reformed gas feeding part, wherein said carbon monoxide shifting catalyst body comprises a carrier composed of at least one metal oxide and/or composite metal oxide having a BET specific surface area of 10 m²/g or more and Pt supported thereon.

It is preferable that above-mentioned metal oxide and/or composite metal oxide is an oxide of at least one selected from the group consisting of Mg, Al, Si, Ca, Ti, Cr, Fe, Zn, Y, Zr, Nb, Mo, Sn, Ba and lanthanoid. Further, in concrete, for example, alumina, silica, silica alumina, zirconia, titania and zeolite can be listed.

[0007]

Furthermore, it is preferable that above-mentioned metal oxide contains cerium oxide and that above-mentioned composite metal oxide contains Ce and/or Zr.

Moreover, it is preferable that in addition to Pt, the above-mentioned monoxide shifting catalyst body supports Pd, Rh or Ru in an amount of 0.1 to 0.5% by weight based on Pt.

It is preferable that above-mentioned carrier is constituted of an inorganic metal material with heat-resisting property.

Also, the hydrogen refinement apparatus of the present invention is preferably operated by controlling the temperature of said carbon monoxide shifting catalyst body from 150 to 450°C, and the temperature of the upstream side part of said carbon monoxide shifting catalyst body is higher than that of the downstream side part.

Furthermore, it is preferable that said reformed gas contains 24 to 50% by volume of steam.

[0008]

[Mode for Embodiment the Invention]

The present invention will be described with the following typical embodiments, by referring to drawings.

[0009]

Embodiment 1

Fig. 1 is a schematic longitudinal sectional view showing the constitution of a hydrogen generating apparatus containing a hydrogen refinement apparatus of the embodiment 1 of the present invention. In Fig. 1, a raw material gas feeding part 1 feeds a raw material gas comprising a fuel and steam, and this hydrogen generating apparatus comprises a heat exchange fin 2, a reforming catalyst body 3, a heating burner 4, an exhaust port 5, a carbon dioxide (CO) shifting catalyst body 6, a thermocouple 7, a temperature controller 8, a cooler 9, an air feeding part 10, a CO purifying catalyst body 11 and a reformed gas discharge port 11 (sic.). Further, in order to keep the reaction chamber at constant temperature, the periphery of necessary portions thereof is covered with a heat insulating material composed of ceramic wool (not shown).

[0010]

Herein, the CO shifting catalyst body 6 is prepared by impregnating an alumina carrier in the form of a pellet shown in Fig. 2 with a Pt salt. Further, as the reforming catalyst body 3, a Ni-based catalyst usually used is employed and as the CO purifying catalyst body 11, a Pt-based catalyst is used. It should be noted that the reforming catalyst body 3 and the CO purifying catalyst body 11 are also shown in Fig. 1 for

explanation of the basic mechanism of the hydrogen refinement apparatus of the present invention.

[0011]

Then, operations and characteristics of this embodiment will be described. As the fuel used for generating a reformed gas to be fed to the hydrogen refinement apparatus, there are natural gas, methanol, gasoline and the like, and as the reforming method, there are a steam reforming method in which steam is added, a partial reforming method in which air is added, and the like. Herein, a case in which natural gas is steam-reformed to obtain a reformed gas will be described.

A mixture of natural gas and steam is fed from the raw material gas feeding part 1 and preheated by passing through a route heat-exchanged by the heat exchange fin 2 and, then, allowed to contact with the reforming catalyst body 3. The reforming catalyst body 3 has been heated at 500 to 800°C by the heating burner, and the raw material gas is converted into hydrogen and CO and carbon dioxide at a conversion ratio of approximately 100%.

[0012]

The composition of the reformed gas somewhat changes depending on the temperature of the reforming catalyst body. In terms of the average composition excepting steam, about 80% of hydrogen, about 10% of carbon dioxide and about 10% of carbon monoxide are contained respectively. This reformed gas is fed to the CO shifting catalyst body 6, to cause a reaction

of CO with steam. Since the CO shifting catalyst body functions at about 150 to 450°C while the reforming catalyst body functions at about 500 to 800°C, the thermocouple 7 detects the temperature of the upstream side part of the CO shifting catalyst body 6, and then the temperature controller 8 having feed back mechanism controls the output of a cooling fan attached to the cooler 9, thereby the temperature of the reformed gas is controlled to make the temperature of the CO shifting catalyst body 6 optimum.

The CO concentration of the gas after passing through the CO shifting catalyst body 6 is about 0.5% and, after mixed with air containing an oxygen in an amount corresponding to 3-fold of the CO concentration thereof, the gas is fed to the CO purifying catalyst body 11. CO is removed to 10 ppm or less by the CO purifying catalyst body 11, and then the gas is fed through the discharge port 12 to a fuel cell.

[0013]

Then, the operation theory of the hydrogen generating apparatus containing the hydrogen refinement apparatus of this example will be described. Herein, the CO shifting catalyst body which is the feature of the present invention will be illustrated in detail.

The CO shifting reaction is an equilibrium reaction depending on temperature, and the CO concentration can be decreased further when the reaction is conducted at lower temperature. On the other hand, the reaction rate on the

catalyst is decreased at lower temperature, there exists a temperature at which the CO concentration has the minimum value.

Usually, the copper-based shifting catalyst such as a copper-zinc catalyst and copper-chromium catalyst used as the CO shifting catalyst can cause a CO shifting reaction at around 150 to 250°C and, depending on conditions, the CO concentration can be decreased to about several hundreds to several thousands ppm.

However, the copper-based catalyst has to be activated by passing through of a reduction gas such as hydrogen or reformed gas after filled in a reaction chamber, and the heat resistance of the copper-based catalyst is as low as around 300°C. Therefore, so as not to exceed the heat-resistant temperature by the reaction heat in activation, the reduction gas should be diluted with an inert gas or the like before feeding, or the reaction should be proceeded gradually at a lower flow rate, requiring a longer period of time.

[0014]

Also, in starting-up of an apparatus, heating should be effected slowly over a long period of time so as not to exceed the heat-resistant temperature by surplus temperature increase, and a lot of problems occur in a use with a frequent repetition of starting-up and stopping.

On the other hand, in the hydrogen refinement apparatus of the present invention, a Pt catalyst is used as the CO

shifting catalyst body 6 and has higher heat-resistance as compared with the copper-based catalysts and, therefore, no significant deterioration occur even in the case of high temperatures around 500°C in starting-up of the apparatus. Further, there is no need for activation for a long period of time in a reduction gas like in the case of the copper-based catalyst. Also, even if air is introduced into an apparatus when the apparatus is stopped, no catalyst deterioration occurs as in case of the copper-based catalyst.

Usually, a noble metal catalyst has high activity against various reactions, and exhibits sufficient activity even at a smaller amount of the noble metal supported, as compared with the catalyst using a transition metal such as copper. Further, the noble metal tends to be reduced due to small production heat of the oxide thereof, and generates small amount of heat when activated with a reduction gas. Consequently, it needs no activation over a long period of time while passing a reduction gas as in case of the copper-based catalyst, and can provide sufficient activity only if a reformed gas is allowed to pass for several minutes after filling of the catalyst.

[0015]

Any of noble metal catalysts such as Pt, Pd, Rh and Ru can cause a CO shifting reaction, however, the reaction selectivity thereof is relatively low due to the high activity, and further, a methanization reaction of CO or carbon dioxide

proceeds as the side reaction of the CO shifting reaction, depending on conditions.

When the methanization reaction proceeds, hydrogen is consumed to decrease efficiency of the whole apparatus. Usually, in the temperature range from 150 to 450°C in which the CO shifting reaction is conducted, the methanization reaction proceeds remarkably at higher temperatures, and the methane yield varies also depending on the kind of the noble metal. The reason for this is that a CO adsorption mechanism varies depending on the kind of the noble metal, and the Pd, Rh and Ru having the CO adsorption mechanism facilitating the methanization reaction generate methane at relatively lower temperature, and the temperature range in which a CO shifting reaction proceeds becomes narrow.

Contrary thereto, the Pt catalyst used in the present invention does not easily cause the methanization reaction, and can provide a CO shifting reaction in a wider temperature range.

[0016]

For obtaining sufficient catalyst activity, it is necessary to make the size of a Pt particle smaller and to provide the particle with a lot of active points and, for this purpose, it is preferable that Pt is supported on a metal oxide having a BET specific surface area of 10 m²/g or more. Herein, the BET specific surface area means a specific surface area measured by a known measuring method, in which nitrogen

is adsorbed on a powder. There is no limitation on the upper limit of the BET specific surface area, even if it is 100 to 200 m²/g, or several hundreds m²/g, similar high activity can be obtained.

The metal oxide and/or composite metal oxide, which supports Pt, is preferably an oxide of at least one selected from the group consisting of Mg, Al, Si, Ca, Ti, Cr, Fe, Zn, Y, Zr, Nb, Mo, Sn, Ba and lanthanoid.

[0017]

On the contrary, when a metal oxide of Cu, Mn, Co, Ni and the like which are not included in above-mentioned group is used, the effect of the present invention cannot be obtained due to heat generation by reduction with a reformed gas after filling of the catalyst as the same as in the case of a Cu-based CO shifting catalyst.

It should be noted that when the BET specific surface area of the metal oxide and composite metal oxide is less than 10 m²/g, Pt is not sufficiently adsorbed, the degree of dispersion of Pt decreases, consequently, no sufficient catalyst activity is obtained. Further, when the amount of supported Pt is reduced to decrease the particle size of Pt, the number of active points decreases and sufficient activity is not obtained.

[0018]

Further, for these metal oxides and composite metal oxides, it is preferable to use one selected from alumina,

silica, silica alumina, zirconia, titania and zeolite, particularly from a viewpoint that high activity can be obtained.

This is because these materials are relatively stable against acid or alkalis, and do not change by an acidic or basic Pt salt. If the metal oxide and the like change by a Pt salt, Pt is buried into the metal oxide and the like to reduce the activity.

[0019]

Further, it is more effective that the composite metal oxide is composed of Ce. Ce has effects to suppress a methanization reaction on a Pt catalyst and to improve activity at lower temperatures against the CO shifting reaction. It is more preferable that the addition amount of Ce is larger.

Accordingly, cerium oxide can be mainly used as the metal oxide.

As long as nitrate salts, acetate salts, hydroxides and the like are used as the raw material of Ce, from which oxide can be obtained, there is no specific restriction thereon. However, when the addition amount of Ce is large, the BET specific surface area of metal oxide may be less than 10 m²/g depending on the preparation method, and in this case, high activity cannot be obtained.

[0020]

Further, since cerium oxide itself has relatively lower

heat resistance, the heat resistance is improved by composition with Zr. Namely, composite metal oxides containing Ce and Zr are preferable. There is no specific restriction on the method to incorporate Zr into cerium oxide, and there can be used, for example, a co-precipitation method, sol-gel method, alkoxide method and the like. Further, Zr may be incorporated into cerium oxide, or Ce may be incorporated into zirconium oxide.

[0021]

Further, when one selected from Pd, Rh and Ru is added in an amount of 0.1 to 0.05-fold based on the weight of Pt, further higher activity is obtained. Since these noble metal elements facilitate a methanization reaction, it is difficult that they alone obtain higher ability as the CO shifting catalyst, but composite thereof with Pt can improve the ability of the Pt catalyst. When these noble metals are added in an amount of more than 0.5-fold on the weight of Pt, properties of the added noble metals emerge and the methanization reaction becomes remarkable, preferably, and when less than 0.1-fold based on the weight of Pt, the effect of addition does not appear at all.

[0022]

The hydrogen refinement apparatus of the present invention exhibits particularly high ability if the temperature of a CO shifting catalyst body 6 is controlled from 150 to 450°C. In the CO shifting reaction, the CO

concentration decreases further at a lower temperature due to equilibrium and, at a higher temperature of over 450°C, the CO concentration cannot be fully decreased and an amount of the methane generated increases to reduce the efficiency of hydrogen generation. On the other hand, at a lower temperature, and specifically, less than 150°C, the CO concentration increases from the viewpoint of the reaction rate.

[0023]

Further, when the temperature of the downstream side part of the CO shifting catalyst body 6 is controlled to be lower than that of the upstream side part thereof by cooling the downstream side part of the CO shifting catalyst body 6, particularly high ability is obtained. Since the CO shifting reaction is an exothermic reaction, the reaction heat generated in the upstream side part of the CO shifting catalyst body 6 is transmitted via the reformed gas to the downstream side part. Therefore, the temperature of the downstream side part of the CO shifting catalyst body 6 is easy to be higher, and even if the CO concentration is sufficiently decreased in the upstream side part, the CO concentration increases again in the downstream side part having higher temperature by a reverse reaction. Therefore, by controlling the temperature of the downstream side part to be lower than that of the upstream side part, the reverse reaction can be suppressed.

Herein, the temperature of the upstream side part of the CO shifting catalyst body 6 and the temperature of the downstream side part thereof are average temperatures over the upstream side half and the downstream side half respectively or, in the case of division into the upstream, middle stream and downstream, average temperatures over the upstream and downstream, and, therefore, it is not limited to temperatures of the most upstream part and the most downstream part. Further, when only the temperature of the most upstream part lowers exceptionally by cooling only the most upstream part, the average temperature of the upstream part excepting this part is regarded as the temperature of the upstream part.

[0024]

Further, when the amount of steam contained in a reformed gas is from 24 to 50% by volume, particularly high activity is obtained. It is more preferable from the equilibrium point of view when the content of steam in the reformed gas is higher, and specifically, when it is contained in an amount of 24% by volume or more, the CO concentration sufficiently decreases. On the other hand, when the steam content increases, the flow rate increases to cause a disadvantage in the reaction rate, and specifically, when the content is more than 50% by volume, the CO concentration cannot be decreased sufficiently.

The amount of steam contained in the reformed gas can be controlled by the amount of feeding water since it can be

increased by addition of water at intermediate part between a reforming part and a shifting part.

[0025]

Herein, a carrier is in the form of a pellet, and the CO shifting catalyst body 6 is produced by impregnation of a Pt salt, however, the shifting catalyst body having the same ability can be obtained by coating a slurry of a catalyst body, which had been prepared previously by supporting Pt onto an alumina powder, on a carrier composed of a heat-resistant inorganic metal material such as cordierite, mullite or the like.

In this case, the amount of a metal powder may be decreased to small amount for coating only on the surface. Alternatively, by using a material having strong heat impact-resistance as the carrier, cracking or break of a catalyst caused by heat impact due to starting-up and stopping is inhibited.

[0026]

Further, also the carrier may be in the form of honeycomb as shown Fig. 3 in addition to the pellet form described above. In the case of honeycomb form, geometrical surface area per unit volume increases and contact area between the CO shifting catalyst body and the reformed gas increases, consequently, more efficient reaction can be conducted. It should be noted that in the case of a carrier in the form of a pellet, it is possible that a catalyst is

filled in a column or the like and a reformed gas is passed through it.

Moreover, there is no specific restriction on the catalyst constituting the reforming catalyst body 3, one capable of reforming a fuel such as a noble metal-based catalyst and other transition metal-based catalyst can be widely used. As the fuel and reforming method, other fuels may be used, and a partial reforming method in which a part of a fuel is oxidized by addition of air may be used.

[0027]

[Working Examples]

<<Example 1>>

Metal oxides or composite metal oxides 1 to 34 having compositions shown in Table 1 were molded into the form of a pellet having a diameter of 6 mm and a height of 3 mm and, then, they were impregnated with a platinum salt, and sintered at 500°C for 1 hour in an electric oven to prepare samples 1 to 34. The BET specific surface areas of these samples measured previously are shown in Table 1.

Then, the samples 1 to 34 were used as the CO shifting catalyst body 6 in the hydrogen refinement apparatus shown in Fig. 1, and the catalytic abilities thereof were evaluated.

First, methane, which is the main component of natural gas, was used as a fuel and steam in a volume of 3-fold based on methane was mixed and introduced into the raw material gas feeding part 1. The composition of the reformed gas after

passing through the heated reforming catalyst body 3 excepting steam, was 80% of hydrogen, 11% of CO and 9% of carbon dioxide. The content of steam was measured by the dew point of the reformed gas to find it was 25%. This reformed gas was fed to the CO shifting catalyst body 6, and the CO concentration after passing through the CO shifting catalyst body 6 was measured by gas chromatography.

The results are shown in Table 1.

[0028]

[Table 1]

Sample No.	(Composite) Metal oxide	BET specific surface area (m ² /g)	CO conc. (%)
1	MgO	52	0.30
2	Al ₂ O ₃	121	0.20
3	SiO ₂	84	0.25
4	CaO	32	0.50
5	TiO ₂	93	0.20
6	Cr ₂ O ₃	41	0.30
7	Fe ₂ O ₃	21	0.80
8	ZnO	74	0.40
9	Y ₂ O ₃	42	0.60
10	ZrO ₂	111	0.15
11	NbO ₂	86	0.30
12	MoO ₃	15	0.80
13	SnO ₂	35	0.70
14	BaO	12	0.90
15	La ₂ O ₃	81	0.40
16	Pr ₂ O ₃	75	0.35

- to be continued -

Sample No.	(Composite) Metal oxide	BET specific surface area (m ² /g)	CO conc. (%)
17	Nd ₂ O ₃	88	0.45
18	Sm ₂ O ₃	62	0.40
19	Eu ₂ O ₃	55	0.35
20	Gd ₂ O ₃	45	0.55
21	Tb ₂ O ₃	61	0.70
22	Dy ₂ O ₃	79	0.60
23	Ho ₂ O ₃	75	0.40
24	Er ₂ O ₃	82	0.40
25	Tm ₂ O ₃	77	0.50
26	Yb ₂ O ₃	43	0.65
27	Lu ₂ O ₃	34	0.70
28	Type A zeolite	415	0.20
29	Type X zeolite	253	0.30
30	Type Y zeolite	325	0.25
31	Mordenite	151	0.35
32	ZSM-5	132	0.20
33	Type β zeolite	255	0.30
34	Silica alumina	212	0.15

[0029]

<<Example 2>>

Mixtures of an alumina powder with a cerium nitrate were sintered at 500°C for 1 hour in an electric oven to incorporate Ce into alumina. The ratios of an alumina with Ce were varied to prepare samples 35 to 37 having compositions

shown in Table 1.

These samples were molded into the form of a pellet having a diameter of 6 mm and a height of 3 mm, then, they were impregnated with a platinum salt, and sintered at 500°C for 1 hour in an electric oven in the same manner as in Example 1 to prepare samples 35 to 37.

Each of them was filled into the hydrogen refinement apparatus shown in Fig. 1 as the CO shifting catalyst body 6, the reformed gas was fed, and the CO concentration after passing through the CO shifting catalyst body 6 was measured by gas chromatography, in the same manner as in Example 1. The results are shown in Table 2.

[0030]

<<Example 3>>

Ammonia was added to an aqueous solution of cerium nitrate to cause precipitation, and the product was sintered in an electric oven at 500°C for 1 hour to prepare cerium oxide which is a sample 38. Then, zirconyl nitrate and cerium nitrate were mixed varying the ratio, and ammonia was added thereto for precipitation to prepare samples 39 and 40.

These samples were molded into the form of a pellet having a diameter of 6 mm and a height of 3 mm, then, they were impregnated with a platinum salt, and sintered at 500°C for 1 hour in an electric oven in the same manner as in Example 1 to prepare samples 38 to 40. Each of them was filled into the hydrogen refinement apparatus shown in Fig. 1

as the CO shifting catalyst body 6, the reformed gas was fed, and the CO concentration after passing through the CO shifting catalyst body 6 was measured by gas chromatography, in the same manner as in Example 1. The results are shown in Table 2.

This hydrogen refinement apparatus was operated for 20,000 hours, and the CO concentration after passing through the CO shifting catalyst body 6 was measured again, to find that the CO concentrations after passing through the CO shifting catalyst bodies 6 when the samples 38, 39 and 40 were used were 0.19%, 0.15% and 0.15% respectively.

[0031]

[Table 2]

Sample No.	(Composite) Metal oxide	BET specific surface area (m ² /g)	CO conc. (%)
35	Al ₉ CeO _x	115	0.18
36	Al ₅ Ce ₅ O _x	100	0.17
37	Al ₃ Ce ₇ O _x	90	0.16
38	CeO ₂	80	0.13
39	Ce ₉ ZrO _x	85	0.14
40	Ce ₇ Zr ₃ O _x	90	0.15

[0032]

<<Comparative example 1>>

The samples 41 to 45 shown in Table 1 were prepared by heating alumina in an electric oven. These samples were molded into the form of a pellet having a diameter of 6 mm and

a height of 3 mm, then, they were impregnated with a platinum salt, and sintered at 500°C for 1 hour in an electric oven in the same manner as in Example 1 to prepare samples 41 to 45.

Each of them was filled into the hydrogen refinement apparatus shown in Fig. 1 as the CO shifting catalyst body 6, the reformed gas was fed, and the CO concentration after passing through the CO shifting catalyst body 6 was measured by gas chromatography, in the same manner as in Example 1. The results are shown in Table 3.

[0033]

[Table 3]

Sample No.	(Composite) Metal oxide	BET specific surface area (m ² /g)	CO conc. (%)
41	Al ₂ O _x	0.9	9.5
42	Al ₂ O _x	9.5	1.8
43	Al ₂ O _x	6	5
44	Al ₂ O _x	0.9	9.5
45	Al ₂ O _x	8.5	3.0

[0034]

<<Example 4>>

Alumina, sample 2 produced in Example 1 was molded into a pellet having a diameter of 6 mm and a height of 3 mm, then, this was impregnated with a mixture prepared by mixing a platinum salt with a Pd salt, Rh salt or Ru salt in given ratio based on the platinum salt, these were sintered in an

electric oven at 500°C for 1 hour to prepare samples 46 to 60 shown in Table 2. These samples 46 to 60 were used as the CO shifting catalyst body 6 in the hydrogen refinement apparatus shown in Fig. 1, and evaluated, in the same manner as in Example 1. The results are shown in Table 4.

[0035]

[Table 4]

Sample No.	Noble Metal added	Weight per 1 g of Pt	CO conc. (%)	Methane conc. (%)
46	Pd	0.08	0.20	0.01
47	Pd	0.1	0.17	0.01
48	Pd	0.3	0.15	0.02
49	Pd	0.5	0.16	0.04
50	Pd	0.6	0.50	1.8
51	Rh	0.08	0.20	0.01
52	Rh	0.1	0.18	0.01
53	Rh	0.3	0.17	0.04
54	Rh	0.5	0.13	0.08
55	Rh	0.6	0.60	3.01
56	Ru	0.08	0.20	0.01
57	Ru	0.1	0.15	0.01
58	Ru	0.3	0.13	0.04
59	Ru	0.5	0.16	0.09
60	Ru	0.6	0.80	4.05

[0036]

<<Example 5>>

The sample 2 comprising platinum supported by the alumina pellet in Example 1 was filled in the hydrogen

refinement apparatus shown in Fig. 1 as the CO shifting catalyst body 6. 50 Liter/min of methane (sic.) and 150 liter/min of steam were introduced at the raw material gas feeding part 1, and they were heated by the heating burner 4 so that the temperature of the reforming catalyst body 3 reached about 800°C to cause reaction. The produced gas after passing through the reforming catalyst body 3 was measured by gas chromatography to find that it contained, excepting steam, about 80% of hydrogen, about 11% of CO, about 9% of carbon dioxide, and 300 ppm of methane. When this reformed gas was passed through the CO shifting catalyst body 6, the CO concentration changed to about 0.20%, and then air was introduced through the air feeding part 10 so as to obtain an oxygen concentration of 2% to cause a reaction over the CO purifying catalyst body 11, consequently, a CO concentration was 5 ppm.

The hydrogen generation apparatus was once stopped, and started-up again. Further, this stopping and starting-up operation was repeated 1,200 times, and the reformed gas composition was measured to find that the CO concentration after passing through the reforming catalyst body 3 was 11%, which had not changed, and after passing through the CO shifting catalyst body 6, the CO concentration was 0.22%, and after passing through the CO purifying catalyst body 11, it was 6 ppm.

[0037]

<<Comparative Example 2>>

A commercially available copper-zinc-based CO shifting catalyst in the form of a pellet having a diameter of 6 mm and a height of 3 mm was filled in the hydrogen refinement apparatus shown in Fig. 1 as the CO shifting catalyst body 6 in the same manner as in Example 1. 50 Liter/min of methane (sic.) and 150 liter/min of steam were introduced at the raw material gas feeding part 1, and they were heated by the heating burner 4 so that the temperature of the reforming catalyst body 3 reached about 800°C to cause reaction. The produced gas after passing through the reforming catalyst body 3 was measured by gas chromatography to find that it contained, excepting steam, about 80% of hydrogen, about 11% of CO, about 9% of carbon dioxide, and 300 ppm of methane. When this reformed gas was passed through the CO shifting catalyst body 6, the CO concentration changed to about 0.11%, and air was introduced through the air feeding part 10 so as to obtain an oxygen concentration of 2% to cause a reaction over the CO purifying catalyst body 11, consequently, a CO concentration was 1 ppm.

The hydrogen generating apparatus was once stopped, and started-up again. This stopping and starting-up movement was repeated 1,200 times, and the reformed gas composition was measured to find that the CO concentration after passing through the reforming catalyst body 3 was 11%, which had not changed, and after passing through the CO shifting catalyst

body 6, the CO concentration was 1.52%, and after passing through the CO purifying catalyst body 11, it was 520 ppm.

[0038]

[Effects of the Invention]

As apparent from comparison of above-mentioned evaluation results between the apparatus of the examples and that of comparative examples, the present invention can provide a hydrogen refinement apparatus wherein the heat resistance of a CO shifting catalyst body is improved, and which operates stably even if stopping and starting-up of the apparatus is repeated.

[BRIEF EXPLANATION OF THE DRAWINGS]

[FIG.1]

A schematic longitudinal sectional view showing the constitution of a hydrogen generating apparatus including a hydrogen refinement apparatus in embodiment 1 of the present invention.

[FIG.2]

A schematic perspective view of carriers in the form of a pellet.

[FIG.3]

A schematic perspective view of a carrier in the form of honeycomb.

[Explanation of Reference Numerals]

1 Raw material gas feeding part

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提出日 平成11年 4月22日

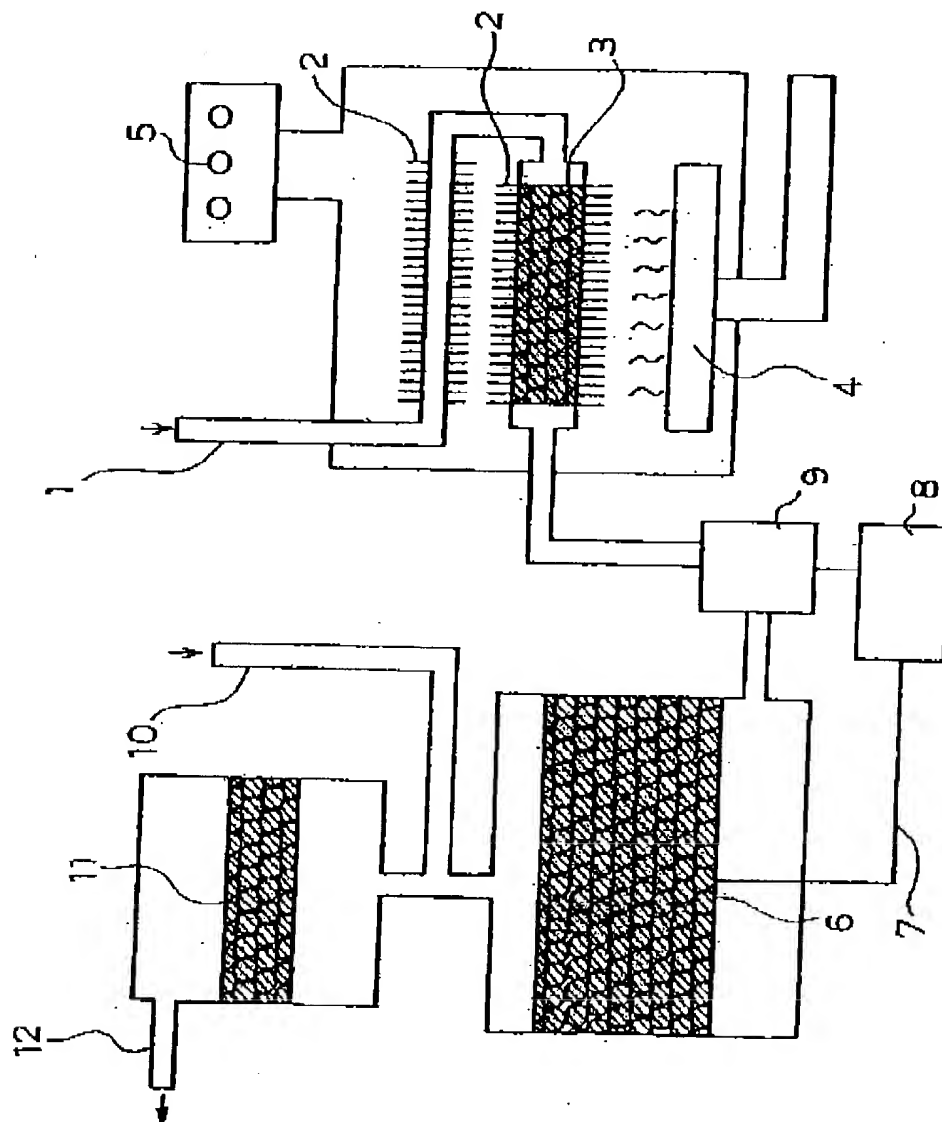
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【書類名】

図面 [DOCUMENT NAME] Drawings

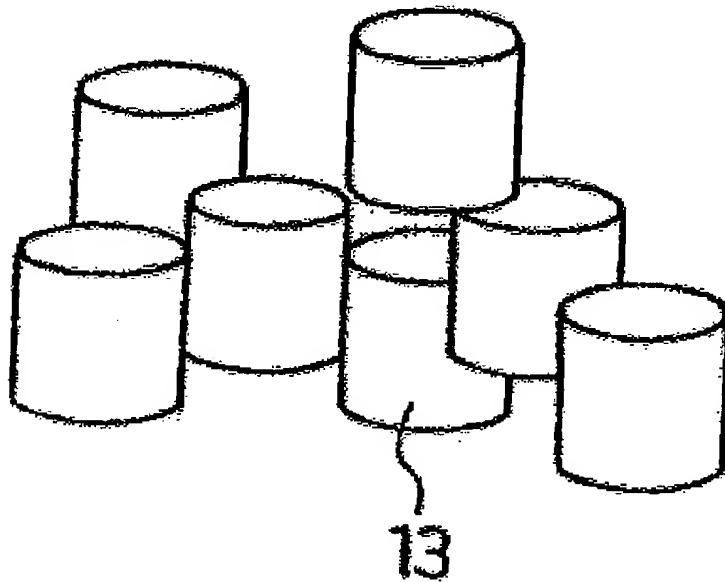
【図1】 [FIG. 1]



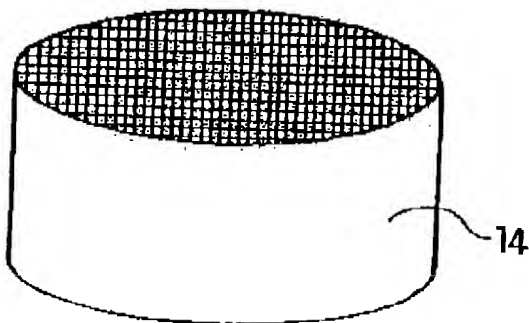
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【図2】 [FIG. 2]



【図3】 [FIG. 3]



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(Translation)

[DOCUMENT NAME] Abstract

[ABSTRACT]

[OBJECTIVE] In a hydrogen refinement apparatus which reduces a CO concentration in a reformed gas containing at least hydrogen gas, CO and steam, by CO shifting reaction, it was difficult to operate it stably for a long period of time when stopping and starting-up was repeated. Also, it was difficult to start the apparatus at a short period of time.

[SOLVING MEANS] A hydrogen refinement apparatus comprising a feeding part for a reformed gas containing at least a hydrogen gas, a carbon monoxide and steam, and a reaction chamber equipped with a carbon monoxide shifting catalyst body positioned downstream from said reformed gas feeding part, wherein said carbon monoxide shifting catalyst body comprises a carrier composed of at least one metal oxide and/or composite metal oxide having a BET specific surface area of $10 \text{ m}^2/\text{g}$ or more and Pt supported thereon.

[SELECTED DRAWING] None

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